



Research Article

Synthesis and Evaluation of ABO_3 Perovskites ($\text{A}=\text{La}$ and $\text{B}=\text{Mn}$, Co) with Stoichiometric and over-Stoichiometric Ratios of B/A for Catalytic Oxidation of Trichloroethylene

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Abstract

In this contribution, perovskite catalysts (ABO_3) were probed that site A and site B were occupied by lanthanum and transition metals of manganese or cobalt, respectively, with stoichiometric ratios as well as 20 % over-stoichiometric ratios of B/A . The perovskite samples were synthesized using a gel-combustion method and characterized by BET, XRD, SEM and O_2 -TPD analyses. After mounting in a fixed bed reactor, the catalysts were examined in atmospheric pressure conditions at different temperatures for oxidation of 1000 ppm trichloroethylene in the air. Evaluation of over-stoichiometric catalysts activity showed that the increased ratio of B/A in the catalysts compared to the stoichiometric one led to BET surface area, oxygen mobility, and consequently catalytic performance improvement. The lanthanum manganite perovskite with 20 % excess manganese yielded the best catalytic performance among the probed perovskites. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Oxidation; Volatile organic compound; Perovskite; Gel-combustion; Catalyst

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1. Introduction

Volatile organic compounds are an important class of atmospheric pollutants in all urban and industrial areas. The pollutants can be classified through two types: indoor and outdoor perspectives. In the indoor environment, volatile organic compounds are produced in many industries, including petrochemical and

paint industries [1]. The largest human resources of the organic gases are related to the vehicle exhausts followed by emissions of power plants and the use of solvents [2]. Many organic compounds are toxic, carcinogenic, mutagenic and responsible for allergic symptoms such as asthma or eczema as well as formation of smog and ozone depletion [1]. More volatile organic compounds, especially chlorinated volatile organic compounds are widely produced in industries as solvents, and as chemicals in the plastics industry, synthetic resins and so forth. Trichloroethylene that is probably one of the most

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common chlorinated volatile organic compounds (CVOCs) and is produced in many above-mentioned industries is resistant against dechlorination due to the presence of a double bond beside the chlorine atoms [3]. Catalytic oxidation is one of the most common used technique for controlling emissions of volatile organic compounds. The activity of the catalyst in this process depends on the type of the volatile organic compound in the gas mixture, the pollutant concentration and so on. Poisoning, deactivation, and sensitivity to heat or mass transfer limitations are among the factors restricting catalytic oxidation activity [2]. Catalysts utilized in the catalytic oxidation of volatile organic compounds are assorted into two major categories: noble metals (Pt, Pd, Rh, Au, etc.) and transition metals (Co, Mn, Cu, Fe, Ni, etc.). Noble metals possess higher catalytic activity than other metals. However, their utilization suffers from their rather high price. Moreover, the deterioration of noble metals occurs as being exposed to chlorine, phosphorus and halogenated compounds in the oxidation of volatile organic compounds reaction [2].

Among the comparatively cheap catalysts that are proposed, perovskites exhibited promising results for the oxidation of volatile organic compounds [4]. Essentially, perovskites are a group of isomorphous compounds with the structural formula of ABO_3 that are cube-shaped. In these compounds, 12 A (larger cations) and 6 B (smaller cations) are coordinated by oxygen anions. Each oxygen atom is surrounded by two cations in position B and four cations in position A [5]. Elements occupying site A in the perovskite structure are mainly lanthanoids and/or alkaline earth metals and site B elements are transition metals [6].

Perovskites possess relevant properties that make them catalytically appealing. These properties include stability of various valence states of transition metals ions (site B) in perovskite structure, the presence of structural defects, non-stoichiometric structures in site A and B and in the amount of oxygen in the structure, high mobility of oxygen, high thermal stability, low cost and no poisoning by sulfur, phosphorus and halogens [4]. Oxidation activity of perovskite catalysts is determined primarily by the kind of the element in Site B [7]. Perovskite catalytic activity of ABO_3 for oxidation of carbon monoxide and hydrocarbons such as propane and methanol shows that the catalytic activity varies as: $\text{LnCoO}_3 > \text{LnMnO}_3 \gg \text{LnFeO}_3$ [8]. In some reports, Co- and Mn- containing

catalysts, exhibited comparable activities [9,10].

Possessing general structure of ABO_3 , perovskites are also reported having non-stoichiometric defects. These defects can be anionic or cationic. Few research groups dealt with non-stoichiometric examination of site B/A in the perovskites. " $\text{La}_{1-\varepsilon}\text{Mn}_{1-\varepsilon}\text{O}_3$ " notation instead of " $\text{LaMnO}_{3+\delta}$ " was suggested for the stoichiometric lanthanum manganite perovskite, where $\varepsilon=\delta/(3+\delta)$ [11]. This notation admitted fully occupied oxygen lattice and cation vacancies that represents real unit of the hexagonal phase and declined presence of excess (interstitial) oxygen. O'Connell *et al.* [12] suggested the non-stoichiometric perovskites are more active than the stoichiometric ones, due to ease of oxygen release. Esmailnejad *et al.* [5] investigated the impact of over-stoichiometric manganese in lanthanum-manganese nanocatalysts on the reduction of oxidation temperature of exhaust gas emitting from gasoline engines and found that about 20 % additional Mn increases the activity and resistance of the catalyst.

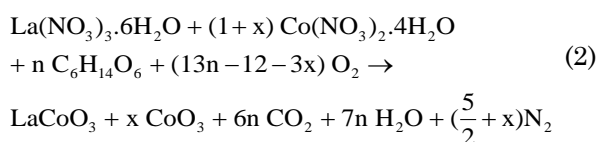
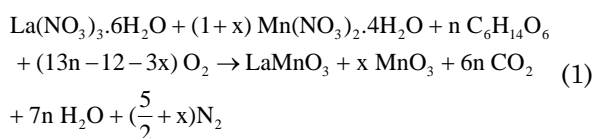
This paper aims to achieve an efficient perovskite for oxidative removal of trichloroethylene. This compound is one of the major pollutants in some petrochemical industry and is considered as a dangerous carcinogen in the International Agency for Research on Cancer classification and the Environmental Protection Agency [13]. Therefore, we studied activity of LaBO_3 (B = Mn and Co) in two stoichiometric and over-stoichiometric states of site B to A (B/A= 1.0 and 1.2) in the catalytic aerobic oxidation of 1000 ppm trichloroethylene at different temperatures.

2. Materials and Methods

2.1 Catalyst preparation

$\text{LaMn}_{1+x}\text{O}_3$ and $\text{LaCo}_{1+x}\text{O}_3$ perovskites-type catalysts were synthesized in two stoichiometric ($x=0.0$) and over-stoichiometric ($x=0.2$) states by microwave assisted gel combustion method. In order to prepare the catalysts, calculated amounts of metal nitrate salts (lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)) as oxidizer and sorbitol ($\text{C}_6\text{H}_{14}\text{O}_6$) as organic fuel mixed together. All the used materials were purchased from Merck Company. Stoichiometric ratio of fuel to oxidizer were used in all of the synthesis. Then, 2 mL of deionized water was added to the mixture, and mixing operation was conducted on a hot

plate at ~130 °C for 15 minutes so that a completely homogeneous and gel-like mixture was obtained. In order to perform the combustion operation, the mixture was placed in the microwave (850 watts) with 100 % power, less than 20 seconds. After combustion and ignition that were followed by releasing a large quantity of gases, the resulting powder was calcined in air atmosphere at 600 °C for 5 hours and sieved to particle size of 0.152-0.251 mm (60-100 mesh size). The combustion synthesis reactions of $\text{LaMn}_{1+x}\text{O}_3$ and $\text{LaCo}_{1+x}\text{O}_3$ perovskites are as follows:



2.2 Characterization of catalysts

X-ray powder diffraction (XRD) analyses were investigated for the crystalline structures of the catalysts by a Philips PW1800 diffractometer using Cu-K α radiation. Diffraction intensity was measured to be $20^\circ < 2\theta < 70^\circ$ for all samples with the step size of 0.03° and a count time of 2 seconds per each step. The resulting spectra were detected by comparing with data in the Joint Committee on Powder Diffraction Standards (JCPDS). The average size of the synthesized crystals (d_{XRD} , nm) was calculated by Debye-Scherrer equation:

$$d_{\text{XRD}} = \frac{k\lambda}{\beta \cos(\theta)} \quad (3)$$

where b is the true half-peak width, l is the wavelength of the used X-ray, and q is the angle between diffracted and input rays.

The morphology and particle size of the catalysts was determined by SEM analysis using TESCAN Vega device. The specific surface areas (S_{BET}) of the catalysts were determined by Nova Station A manufactured by Quantachrome NovaWin2 Company. Specific surface area was determined at the liquid nitrogen temperature, which was obtained by adsorption and desorption isotherms of nitrogen. The O_2 -temperature programmed desorption (O_2 -TPD) analysis was investigated by a multi-purpose device of CHEMBET-3000 Model man-

ufactured by Quantachrome Company. Prior to each TPD run, the catalyst was first preheated up to 300 °C under a flow of oxygen and was kept at this temperature for 1 h. Then, the catalyst under the above-mentioned gas flow was cooled down to the room temperature. After ending this process, oxygen was absorbed on the catalyst surface and the catalyst is fully oxidized. Then, the catalyst was then flushed with a flow helium at room temperature for a period of 30 min to clean the catalyst surface from the weakly and physically bounded oxygens. Eventually, the catalyst temperature was increased to 1000 °C with the rate of 10 °C/min under helium flow (as neutral environment) and desorbed oxygens was detected by a thermal conductivity detector.

2.3 Catalyst activity evaluation

An experimental setup was developed for testing the catalysts activity for trichloroethylene oxidation and shown in Figure 1. In order to examine the activity of the catalysts for the catalytic oxidation experiments, 0.1 g of each catalyst was placed in the reactor on a small piece of acid washed quartz wool. The fixed bed reactor was made from quartz with the inner and outer diameter of 7 and 9 mm, respectively. An electrical furnace was used to heat the reactor around the reactor. Furnace temperature was adjusted by a temperature controller. K-type thermocouples were used for monitoring and controlling temperature of the reactor.

The catalyst was first heated up to 600 °C with heating rate of 10 °C/min under a flow of air (30 cc/min). It should be noted that prior to testing, each of mass flow controllers are calibrated for the specific gas. Then, the reactor temperature was lowered and exhaust gases from the reactor were analyzed by Agilent 6890N gas chromatography (equipped with FID and a CP-Sil 52 CB column) at specified temperatures and after establishment of steady state conditions at any temperature. All the experiments were carried out at fixed concentration of trichloroethylene (1000 ppm in air) and gas hourly space velocity (GHSV) of 8500 h⁻¹. The trichloroethylene conversion was calculated based on the inlet and outlet concentration:

$$\text{Conversion}(\%) = \frac{[\text{VOC}]_{\text{in}} - [\text{VOC}]_{\text{out}}}{[\text{VOC}]_{\text{in}}} \times 100 \quad (4)$$

3. Results and Discussion

3.1 Catalyst characterizations

3.1.1 X-ray Diffraction

In order to study the crystalline structure of the synthesized catalysts including LaMnO_3 , LaCoO_3 , $\text{LaMn}_{1.2}\text{O}_3$, and $\text{LaCo}_{1.2}\text{O}_3$, the XRD patterns were acquired that are shown in Figure 2a and b. In the LaMnO_3 sample, the observed peaks are attributed to the presence of lanthanum-manganese perovskite (JCPDS 32-0484). This indicates that the perovskite is formed in a single-phase process and other probable compounds, such as manganese or lanthanum oxides were not detectable by XRD technique. In the case of LaCoO_3 sample, the comparison of this spectra (Figure 2b) with JCPDS charts indicates that this sample is essentially lanthanum cobaltite perovskites type mixed oxides. Therefore, the formation of perovskite structure is also confirmed and other ingredients such as cobalt or lanthanum oxides were not observed. This observation is supported by other studies [14].

Figures 2c and d show XRD spectrum of perovskites with the 20% over-stoichiometry of Mn and Co ($\text{LaMn}_{1.2}\text{O}_3$ and $\text{LaCo}_{1.2}\text{O}_3$), respectively, that did not differ with the spectrum of the stoichiometric perovskites (Figures 2a and b). Thus, it could be concluded that the additional cobalt and manganese oxides in the over-stoichiometric perovskites are either amorphous or they are scattered as very small crystals in the perovskite. Consequently, they are not detectable by XRD technique. In this regard, Van Roosmalen *et al.* reported the exclusive existence of perovskite structure in XRD spectrum for lanthanum-manganese perovskite

with La/Mn ratio between 0.908 and 1.202 at 1123 K in air [15].

The average crystalline size of the synthesized perovskites (d_{XRD}) are calculated by Debye-Scherrer equation (Equation 1) and shown in Table 1. As exhibited in Table 1, the average sizes of the synthesized crystals range from 14 to 23 nm. Perovskites are reported possessing d_{XRD} equal or even higher than our results. For instance, Siquin *et al.* [16] studied on the LaMnO_3 and LaCoO_3 perovskites synthesized by sol-gel method and reported the occurrence of crystalline with mean size of 20 nm and 67 nm, respectively.

In many instances, particle size diversity is a consequence of different calcination temperature with the elaboration method being identical. In the other hand, parameters such as perovskite synthesis method as well as precursor types play undeniable role in determining textural and structural properties of the prepared materials.

3.1.2 SEM

Morphology of the synthesized catalysts was analyzed by SEM. Figure 3a and 3b show LaMnO_3 and LaCoO_3 perovskites, respectively. It is evident that the synthesized perovskites have a spongy and porous structure with large voids. Formation of these features is attributed to the escape of a large amount of gas during the combustion of organic species used in the preparation process that in agreement with other studies [17].

3.1.3 BET analysis

Specific surface area of the synthesized catalysts was determined by BET technique as

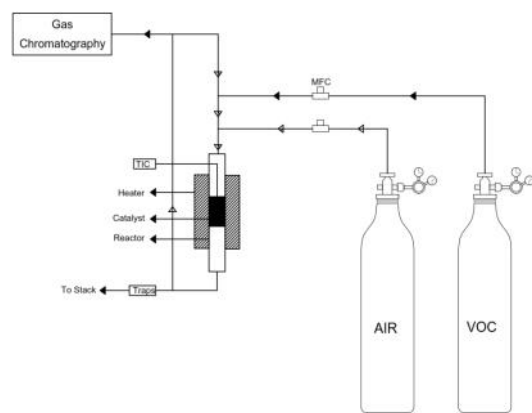


Figure 1. Schematic diagram of the experimental setup for catalytic oxidation of trichloroethylene

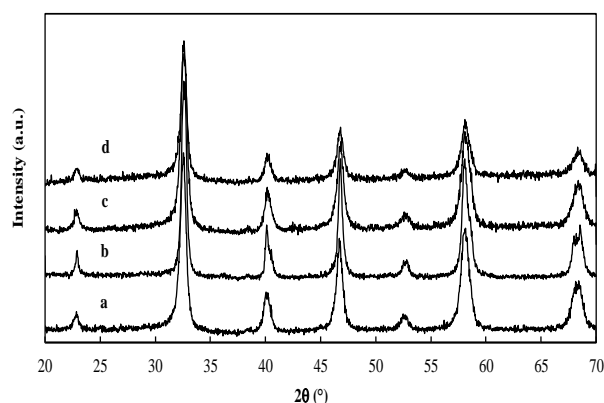


Figure 2. XRD patterns of fresh (a) LaMnO_3 , (b) LaCoO_3 , (c) $\text{LaMn}_{1.2}\text{O}_3$, and (d) $\text{LaCo}_{1.2}\text{O}_3$ perovskites synthesized by gel-combustion method

shown in Table 1. Specific surface area of stoichiometric perovskites of LaMnO_3 and LaCoO_3 equals to 16 and 13 m^2/g , respectively. Generally, low amounts of specific surface areas have been reported for perovskites in the literature [18-20]. Taran *et al.* [21] found that the specific surface area of the perovskite LaMnO_3 prepared by Pechini method and calcined at 900°C being about 3.2 m^2/g . Sinquin *et al.* [16] studied perovskites synthesized by sol-gel method. This study showed specific surface area of LaCoO_3 and LaMnO_3 being 1.17 and 9.2 m^2/g , respectively, revealing the dependence of the particle size and specific surface area of the samples to the synthesis method. In addition, other studies such as Álvarez-Galván *et al.* [22] and Ziaei *et al.* [17] synthesized LaMnO_3 with distinct synthesis methods and reported that the specific surface area of the perovskite is largely affected by the synthesis method and gel-combustion is the one of the best methods in this area. Therefore, the recipe utilized in our paper led to a praiseworthy result for the specific surface area.

Elaboration of over-stoichiometric perovskites is accompanied by some alterations in the structure of catalysts that are reflected as significant specific surface area raise as com-

pared to stoichiometric ones. The BET surface area increases from 16 to 24 m^2/g with the 20% excess Mn for lanthanum manganite perovskite. Similarly, the observation stands for LaCoO_3 and $\text{LaCo}_{1.2}\text{O}_3$ possessing specific surface areas of 13 and 18 m^2/g , respectively. Therefore, it could be concluded that over-stoichiometric addition of Mn and Co to the perovskite structure led to about 50 % and 30 % increase at BET specific surface area, respectively.

3.1.4 O_2 -TPD

Figure 4 (a) shows oxygen mobility in the synthesized perovskites acquired by O_2 -TPD analysis. Two distinct characteristic peaks are observable in O_2 -TPD profiles of the probed perovskites: (1) The earliest peak locating in the range of $300\text{--}700^\circ\text{C}$ corresponds to a oxygen. This is attributed to the oxygen adsorbed on the anionic vacancies existing on the surface with rather more mobility. (2) The second peak above 700°C is related to b oxygen. This is appointed to the oxygen species with stronger bonds that are usually released from the perovskite lattice bulk. Therefore, the release of b oxygen requires elevated temperatures as comparing to a oxygen species. It is worthwhile to mention that the amount of the oxygen released in the second peak ($> 700^\circ\text{C}$) usually does not play an important role in the oxidation of trichloroethylene because this compound totally oxidizes at temperatures below 600°C . Thus, the first peak that plays an important role in the catalytic activity, is calculated for perovskites (LaMnO_3 , LaCoO_3 , $\text{LaMn}_{1.2}\text{O}_3$ and $\text{LaCo}_{1.2}\text{O}_3$). The total amount of a-oxygen desorbed ($\text{mmol O}_2/\text{mol catalyst}$), calculated from the first peak area of the catalysts is calculated and plotted in Figure 4b. As seen

Table 1. Crystallites average size (d_{XRD}) and BET specific surface areas (S_{BET}) of as prepared perovskite by gel-combustion method and calcined at 600 in air

Catalyst	d_{XRD} (nm)	S_{BET} (m^2/g)
LaMnO_3	16	16
LaCoO_3	23	13
$\text{LaMn}_{1.2}\text{O}_3$	14	24
$\text{LaCo}_{1.2}\text{O}_3$	20	18

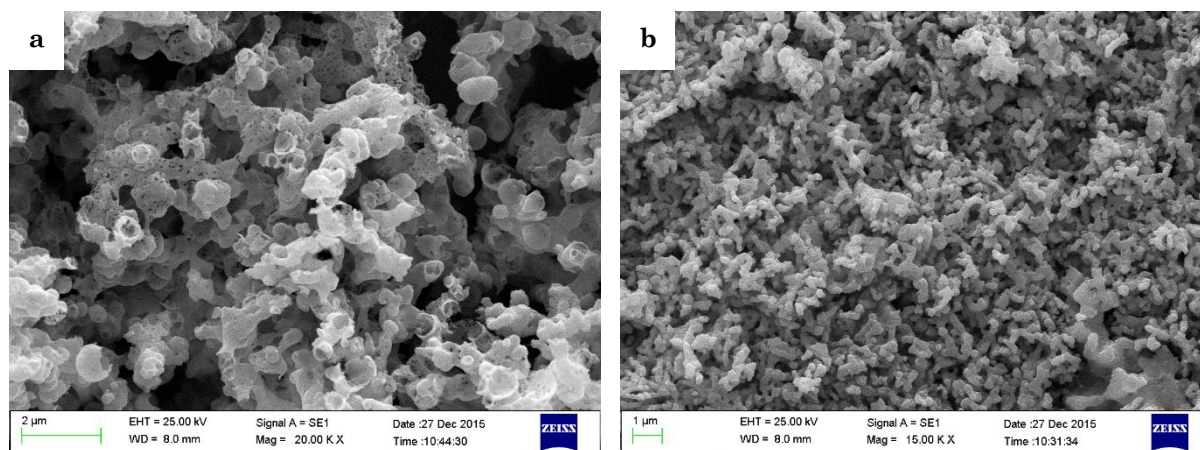


Figure 3. SEM micrographs of the (a) LaMnO_3 , and (b) LaCoO_3 synthesized by gel-combustion method

in the Figure 4, mobility of oxygen in the catalysts studied are as follows: $\text{LaMn}_{1.2}\text{O}_3 > \text{LaMnO}_3 > \text{LaCo}_{1.2}\text{O}_3 > \text{LaCoO}_3$.

As can be noted, oxygen mobility is higher in Mn-containing perovskites than the ones containing Co, which is in synchronization with previous studies. For instance, O_2 -TPD graph in Nitadori *et al.*'s study [8] showed that mobility of oxygen at temperatures range of 150-500 °C in LaMnO_3 is higher than that of LaCoO_3 . Also, oxygen mobility in O_2 -TPD investigation in the over-stoichiometric perovskites ($x=0.2$) is higher than stoichiometric ones ($x=0.0$) for the both lanthanum manganite and lanthanum cobaltite perovskites. Most studies indicated that catalytic activity is directly proportional to the oxygen mobility. Spinicci *et al.* [14] compared perovskites LaBO_3 ($B=\text{Mn, Co}$) for catalytic oxidation of benzene and concluded that LaMnO_3 shows higher activity due to more surface oxygen species (based on the results of TPD analysis).

Another study investigated perovskite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ in normal oxidation of butane. The results demonstrated that the augmented activity of the catalyst with Sr substitution is in synchronization with increased amount of oxygen disposed in the O_2 -TPD studies [23]. Li *et al.* [24] used LaMnO_3 and $\text{LaMn}_{0.95}\text{B}_{0.05}\text{O}_3$ ($B=\text{Pd, Pt, and Rh}$) perovskites in the oxidation of methanol and reported that substitution of Mn by Pt ($\text{LaMn}_{0.95}\text{Pt}_{0.05}\text{O}_3$) showed the best results in oxidation of methanol and the highest oxygen mobility in O_2 -TPD analyses.

3.2 Evaluation of catalytic activity in the oxidation of trichloroethylene

3.2.1 Comparison of LaMnO_3 and LaCoO_3 stoichiometric perovskites

Figure 5 shows oxidation activity of the stoichiometric perovskite catalysts, LaMnO_3 and LaCoO_3 , for oxidation of 1000 ppm trichloroethylene in the air. As can be noted in the Figure 5, the existence of Mn in Site B of perovskite LaBO_3 instead of Co leads to enhanced catalytic performance in oxidation of trichloroethylene. This may be due to higher specific surface area of the catalysts (Table 1), and superior oxygen mobility (Figure 4b) in the perovskite LaMnO_3 . Other researchers have found similar results: for instance, Spinicci *et al.* [14] compared LaMnO_3 and LaCoO_3 perovskites prepared by citrate method and concluded that LaMnO_3 is more active than LaCoO_3 in the oxidative catalytic removal of chlorinated volatile organic compounds.

For accuracy, catalytic activity evaluation of the catalysts was repeated three times to obtain the average value which are reported. Error bars indicate maximal and minimal conversions measured at each temperature in reproducibility experiments under identical reaction conditions. The results of error bars are shown in Figure 5. An acceptable error range in all of the catalysts are observed.

Table 2 shows T_{50} and T_{90} , defined as the temperature required to convert 50 % and 90 % of trichloroethylene. Changing Co to Mn in Site

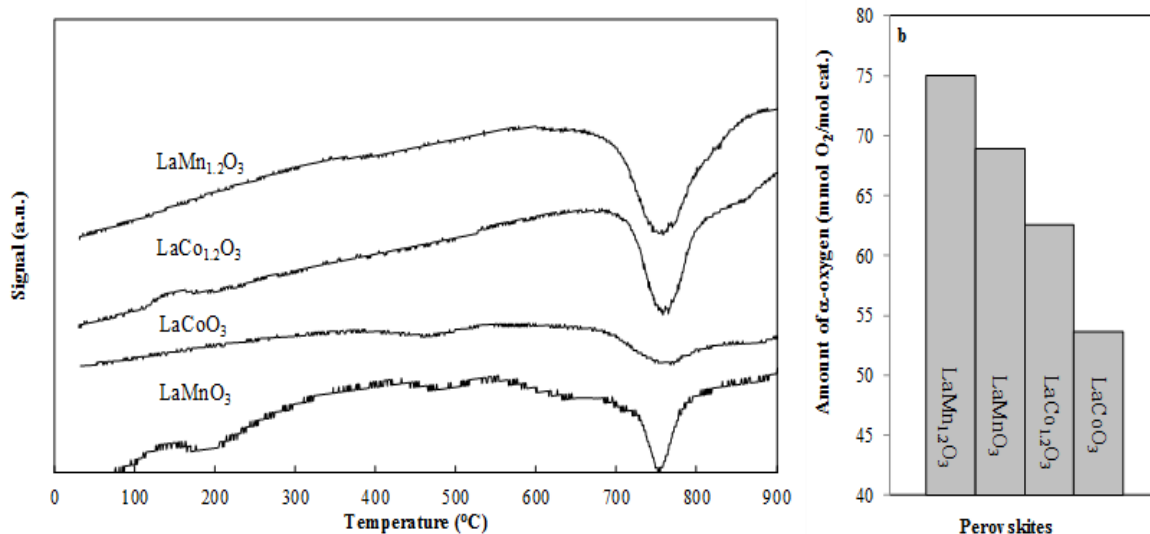


Figure 4. (a) O_2 -TPD profiles and (b) amount of desorbed α -oxygen (mmol O_2 /mol catalyst) of LaMnO_3 , LaCoO_3 , $\text{LaMn}_{1.2}\text{O}_3$, and $\text{LaCo}_{1.2}\text{O}_3$ perovskites synthesized by gel-combustion method and calcined at 600°C

B of perovskite LaBO_3 reduce T_{50} and T_{90} about 50 and 60 °C, respectively.

Several studies were conducted on the oxidation of trichloroethylene using various transition metal catalysts as well as noble metals. The presence of a double bond with chlorine atom enhances the resistance of trichloroethylene ($\text{CHCl}=\text{CCl}_2$) against dehydrochlorination. For example, trichloroethylene degradation using $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts requires high temperatures around 500 °C [23]. Recent researches aiming at oxidative catalytic removal of trichloroethylene has been published; A CeO_2 catalyst which was reported having T_{90} above 500 °C [22], a $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst with T_{90} greater than 520 °C [25], T_{90} of a SO_4ZrO_2 catalyst being equal to 575 °C and the value achieved by a $\text{Pd}/\text{SO}_4\text{ZrO}_2$ catalyst is around 550 °C [26].

3.2.2 Comparison of stoichiometric perovskites with over-stoichiometric ones

Figure 6 depicts the results of the oxidation activity of the synthesized stoichiometric perovskites of LaMnO_3 and LaCoO_3 besides over-stoichiometric perovskites of $\text{LaMn}_{1.2}\text{O}_3$ and $\text{LaCo}_{1.2}\text{O}_3$ for oxidation of 1000 ppm trichloroethylene in the air. It was found that increasing the ratio of Mn/La and Co/La in the lanthanum manganite and lanthanum cobaltite perovskites from 1 to 1.2 leads to the improved catalytic performance in oxidation of trichloroethylene. This observation may be due to higher specific surface area of catalysts (as a consequence of Mn/La ratio increasing, Table 1) as well as higher oxygen mobility (Figure 4b).

Table 2 shows that as compared with stoichiometric LaMnO_3 , a reduction of about 60 and 20 °C for T_{50} and T_{90} , respectively, is ob-

servable for over-stoichiometric $\text{LaMn}_{1.2}\text{O}_3$ perovskite. In the case of LaCoO_3 perovskite, the reductions are 22 and 28 °C, respectively. According to open literature, partial substitution in the B site of the perovskite and/or over-stoichiometry may be responsible for enhanced activities of perovskite through structural changes related to oxygen vacancies or alteration of cation capacities [18,27-28].

Among all the synthesized catalysts, $\text{LaMn}_{1.2}\text{O}_3$ yielded the best activity in trichloroethylene catalytic oxidation. Moreover, BET and O_2 -TPD analyses indicated that specific surface area and oxygen mobility corresponds with $\text{LaMn}_{1.2}\text{O}_3$ was higher than other probed perovskite-type catalysts.

LaMnO_3 is frequently reported being among the most active perovskites that can exist in non-stoichiometric mode in one or two sub-networks. Recent research has shown that non-stoichiometric perovskite with structural defects in Mn is more active than stoichiometric Mn-containing perovskite in oxidation of methane. The creation of such vacancies can increase α oxygen activity of the network and thus catalytic activity enhances. Spinicci *et al.* [11] showed that activity of a non-stoichiometric perovskite with defect in site B is higher than stoichiometric perovskite.

It can be assumed a simple power-law kinetic model for modeling the catalytic oxidation of trichloroethylene (Equation (1):

$$(-r_{\text{TCE}}) = k P_{\text{TCE}}^n \quad (1)$$

where $(-r_{\text{TCE}})$ is the reaction rate of TCE oxidation ($\text{mol kg}_{\text{catalyst}}^{-1} \cdot \text{s}^{-1}$), P_{TCE} is the TCE partial pressure (Pa) and k is the reaction rate constant ($\text{mol kg}_{\text{catalyst}}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-n}$), which is supposed to have an Arrhenius dependence on temperature ($k = A \exp(-E_a/RT)$). Miranda *et al.* [30, 31] have proposed first-order kinetics for the oxidation of trichloroethylene with different catalysts. In the case of first-order kinetics, the integrated kinetic equation is expressed in Equation (2).

$$x_{\text{TCE}} = \frac{kW}{F_{\text{TCE}_0}} \quad (2)$$

where x_{TCE} is the TCE fractional conversion, W the catalyst weight (kg), and F the molar feed flow rate ($\text{mol} \cdot \text{s}^{-1}$). For $\text{LaMn}_{1.2}\text{O}_3$, LaMnO_3 , $\text{LaCo}_{1.2}\text{O}_3$, and LaCoO_3 catalysts, activation energy (E_a) for the zero order reaction are 17.9, 18.3, 19.6, and 20.2 $\text{kJ} \cdot \text{mol}^{-1}$, respectively.

Miranda *et al.* [30,31] have proposed that zero order kinetics model could be related to

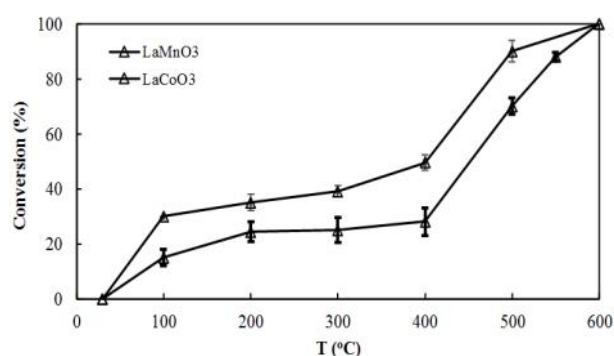


Figure 5. Oxidation of 1000 ppm of trichloroethylene in air on 0.1 g of LaMnO_3 and LaCoO_3 perovskites. Error bars indicate maximal and minimal conversions measured at each temperature in reproducibility experiments under identical reaction conditions

Langmuir-Hinselwood, Eley-Rideal, or Mars-van-Krevelen mechanism models by assuming reaction between strongly adsorbed oxygen and trichloroethylene, reaction of adsorbed trichloroethylene on the surface of catalyst with gas phase oxygen, or interactions of trichloroethylene with an oxygen-rich part of the catalyst, respectively.

Table 2. T_{50} and T_{90} (°C) of as prepared perovskite by gel-combustion method for oxidation of 1000 ppm of trichloroethylene in air

Catalysts	T_{50} (°C)	T_{90} (°C)
LaMnO ₃	400	500
LaCoO ₃	450	560
LaMn _{1.2} O ₃	340	480
LaCo _{1.2} O ₃	428	532

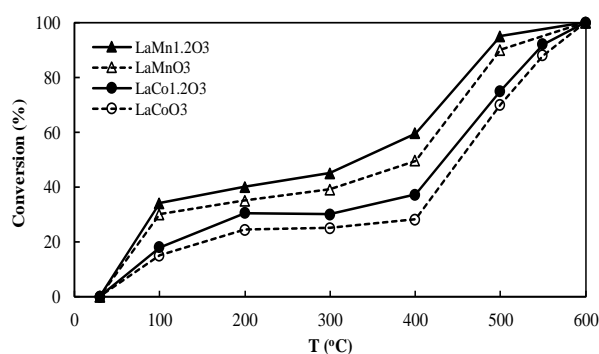


Figure 6. Oxidation of 1000 ppm of trichloroethylene in air on 0.1 g of LaMnO₃, LaCoO₃, LaMn_{1.2}O₃, and LaCo_{1.2}O₃ perovskites

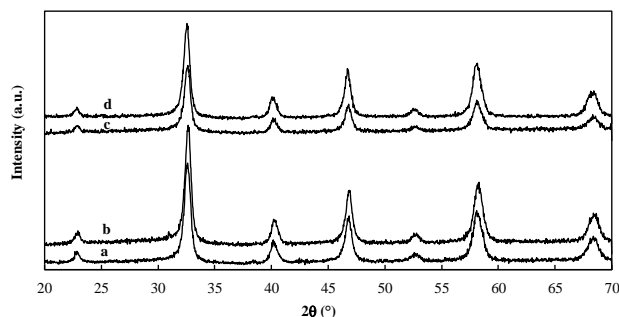


Figure 7. XRD patterns of (a) fresh LaMn_{1.2}O₃, (b) used LaMn_{1.2}O₃, (c) fresh LaCo_{1.2}O₃, (b) used LaCo_{1.2}O₃ after reaction with 1000 ppm of trichloroethylene

3.3 Structural analysis of the used catalysts

XRD spectra of the over-stoichiometric synthesized catalysts acquired after oxidation reaction of 1000 ppm trichloroethylene in the temperature range of 25-600 °C. Figure 7 shows these spectra for fresh and used LaMn_{1.2}O₃ and LaCo_{1.2}O₃ perovskites. The obtained XRD spectra revealed that the fresh and spent samples were nearly the same. Therefore, not only perovskite structure was remained intact during the oxidation reaction, but also no new detectable phase(s) may be formed in the samples, thus the corresponding phases of the probed perovskites are preserved under the reaction conditions. The perovskite structure is maintained because oxygen in the air can be adsorbed on the surface and replenishes the oxygen of the perovskite. Thus, the oxygen in the air plays an important role in maintaining structure of perovskite phase.

4. Conclusions

LaMn_{1+x}O₃ and LaCo_{1+x}O₃ perovskites were synthesized using gel combustion method, stoichiometric (x=0.0) and over-stoichiometric (x=0.2), that employed for oxidation of 1000 ppm trichloroethylene in air. As demonstrated by XRD analysis, the aforementioned perovskites were exclusively consisted of a single phase in order that no other metal oxides were detected. In the case of over-stoichiometric samples, it was found that additional cobalt and manganese oxides may be amorphous or they are scattered as very small crystals in perovskite that are not detectable by XRD technique. Moreover, Mn-containing perovskites compared to perovskites containing Co in both stoichiometric and over-stoichiometric modes exhibited higher specific surface area as well as oxygen mobility. These may lead to the improved catalytic activity of the Mn-containing perovskites. Also over-stoichiometric perovskites possessed enhanced activity in comparison with stoichiometric ones. As T_{50} and T_{90} being equal to 340 and 480 °C, respectively, LaMn_{1.2}O₃ perovskite had superior performance among the investigated catalysts.

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